

Electron Pairing and Chemical Bonds: Bonding in Hypervalent Molecules from Analysis of Fermi Holes

ROBERT PONEC,¹ ANTHONY J. DUBEN²

¹*Institute of Chemical Process Fundamentals, Czech Academy of Sciences, Prague 6, Suchbátka, 165 02, Czech Republic*

²*Department of Computer Science, Southeast Missouri State University, Cape Girardeau, Missouri 63701-4799*

Received 1 September 1998; accepted 23 December 1998

ABSTRACT: Bonding in the hypervalent molecules SF₄, BrF₅, PF₅, and SF₆ was studied using multicenter bond order indices and examination of the eigenvalues and the eigenvectors of the Fermi holes of the constituent atoms. Diagonalization of the Fermi holes provided quantitative validation of Musher's categorization of hypervalency with SF₄ and BrF₅ representative of type I, and PF₅ and SF₆ belonging to type II. The eigenvalues and eigenvectors of type I molecules distinguished between classic two-center two-electron bonds and three-center four-electron bonds, whereas the results of diagonalization for type II molecules demonstrated the presence of substantial reorganization of the valence state of the central atom leading to equivalent bonds and the highest expected symmetry of the molecule. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 760–771, 1999

Keywords: pair density; Fermi hole; chemical bonding; hypervalence

Introduction

The continuing progress in the development of new computational tools of quantum chemistry has reached a stage in which reliable theoretic-

cal calculations have become possible on real, chemically interesting systems making computational chemistry a routine part of chemical research. The increasing accuracy and sophistication of quantum chemical methods used has, however, one unpleasant side effect. The complexity of the wave functions makes their interpretation more difficult. It is harder to find direct links between the results of calculations and classical chemical concepts of bonds, bond orders, valences, VB structures, etc., which chemists usually use. The

Correspondence to: R. Ponec; e-mail: rponec@icpf.cas.cz

Contract/grant sponsor: Grant Agency of the Czech Academy of Sciences, contract/grant number: A4072606/1996; contract/grant sponsor: National Research Council (USA)

development of new computational methods and procedures thus needs to be accompanied by the parallel design of auxiliary methods for interpreting wave functions and for extracting from them the desired structural information. Earlier examples of these efforts in relating modern theory and classical concepts of bond order and valence are described in refs. 1–7.

Our recent studies in which the systematic analysis of pair density and related quantities was introduced^{8–11} as a new efficient way of visualizing molecular structure even in systems with complicated bonding patterns^{12,13} fit into the framework of these efforts. Our aim in this study is to pursue the philosophy of these previous studies and to show that the Fermi holes^{14,15} can be used advantageously as a new means of characterizing bonding in hypervalent molecules. The study is divided into two parts. In the first part, the theoretical background underlying the introduction of the Fermi hole will be reviewed briefly. In the second part, the new theoretical technique will be applied to the investigation of the valence states of atoms in molecules with emphasis on the analysis of bonding in hypervalent systems. Although the methodology is at present practically applicable at simple SCF level of theory only, the anticipated effects of including electron correlation will be discussed qualitatively.

Theoretical

Although the methodology of the analysis of the Fermi hole was described thoroughly in our previous studies,^{14,15} it is worthwhile to recapitulate briefly the basic ideas of the approach. The Fermi holes, first introduced by Wigner¹⁶ in the field of solid-state physics, describe the effect of mutual coupling of electrons of the same spin on the behavior of quantum systems. Our aim in this study is to demonstrate the usefulness of the Fermi holes for the analysis of bonding in molecular systems. The definition of the Fermi hole begins with the conditional probability of finding one electron at position r_1 , provided the second (reference) electron is localized at r_2 . This probability is given in terms of pair density $\rho(r_1, r_2)$ by:

$$P_{r_2}(r_1) = \frac{2\rho(r_1, r_2)}{\rho(r_2)} \quad (1)$$

The Fermi hole associated with the reference electron in r_2 is then given by:

$$h_{r_2}(r_1) = \rho(r_1) - P_{r_2}(r_1) \quad (2)$$

where $\rho(r_1)$ is the usual first-order density, which describes the probability of finding the electron at the point r_1 . Here, it should be noted that another closely related definition [eq. (3)], in which the Fermi hole is a negative quantity, is usually preferred:

$$H_{r_2}(r_1) = P_{r_2}(r_1) - \rho(r_1) \quad (3)$$

but this simple rearrangement has no impact on the physics behind the hole. For reasons that will become clear later (possibility to interpret the eigenvalues of the matrix representing the hole as occupation numbers), we prefer, in this study, definition (2), in which the Fermi hole is a positive quantity.

The physical meaning of the Fermi hole is thus that it provides corrected “net” information about the distribution of the first electron of the pair, provided the second (reference) electron is at r_2 . The Fermi hole defined by eq. (2) has been analyzed and discussed by various investigators^{17–22} and their usefulness for the qualitative discussion of bonding was clearly demonstrated. Our aim in this study is to follow up the results of these studies and to demonstrate that the appropriately generalized quantity, the so-called domain-averaged Fermi hole, can be used advantageously as a new, efficient means of characterizing bonding in hypervalent molecules. The idea of introducing the concept of the domain-averaged Fermi hole is very simple and goes back to the original definition of the conditional probability eq. (1). If we release the condition of strict localization of the reference electron in a single point and replace it with a physically much more reasonable condition, allowing it to be found anywhere in some region of space, Ω , the original definition eq. (2) of the Fermi hole is changed to:

$$P_{\Omega}(r_1) = \frac{2\int_{\Omega} \rho(r_1, r_2) dr_2}{\int_{\Omega} \rho(r_2)} \quad (4)$$

Based on this definition, the domain-averaged Fermi hole associated with the reference electron in the region Ω is then defined as:

$$h_{\Omega}(r_1) = \rho(r_1) - P_{\Omega}(r_1) \quad (5)$$

Here, it is necessary to stress that, in our previous studies,^{14,15} the term "integrated Fermi hole" was used for the quantity in eq. (5); however, because this term was a bit confusing, the referee proposed the more appropriate term "domain-averaged Fermi hole."

This averaged Fermi hole satisfies the universal normalization:

$$\int h_{\Omega}(r_1) dr_1 = 1 \quad (6)$$

which holds, irrespective of the form of the region Ω . Although the validity of this equation is not influenced by the actual size and form of the region Ω , it is possible to choose an Ω that is especially useful for chemistry. The choice is based on Bader's idea of partitioning the total electron density into regions associated with individual atoms.²³ Adopting this type of partitioning, the region Ω is identified with the atomic regions of Bader's partitioning. The simplest possibility is to identify Ω with the atomic region of a single atom. This choice will be emphasized in this study. In previous studies^{14,15} we demonstrated that the Fermi hole associated with the atomic region of a single atom provides valuable information about the valence state of that atom in a molecule. The quantity that provides this information is not, however, the Fermi hole [eq. (5)] itself, but rather the "charge-weighted" Fermi hole $g_{\Omega}(r_1)$ related to the original hole by the simple relation:

$$g_{\Omega}(r_1) = N_{\Omega} h_{\Omega}(r_1) \quad (7)$$

where the proportionality factor N_{Ω} is equal to the mean number of electrons in the region Ω :

$$N_{\Omega} = \int_{\Omega} \rho(r_1) dr_1 \quad (8)$$

The philosophy underlying the introduction of these "charge-weighted" Fermi holes is very simple. The "normal" Fermi hole was derived from the conditional probability describing the distribution of the first electron of the pair, provided the other was known to be somewhere in Ω . The localization of a single electron in the region Ω is an artificial act that does not reflect the fact that in the real molecule the region Ω is populated by N_{Ω} electrons, rather than by only one. The proportionality factor in eq. (7) is therefore nothing but a correction for the statistical probability of distribution of electrons in Ω .

In this connection it is perhaps worth mentioning that the quantity, eq. (7), can be obtained alternatively by the appropriate integration of the so-called exchange part of the pair density²⁴:

$$\begin{aligned} g_{\Omega}(r_1) &= \rho(r_1) \int_{\Omega} \rho(r_2) dr_2 - 2 \int_{\Omega} \rho(r_1, r_2) dr_2 \\ &= N_{\Omega} \rho(r_1) - 2 \int_{\Omega} \rho(r_1, r_2) dr_2 \end{aligned} \quad (9)$$

The quantities eqs. (5) and (7) are also closely related to the so-called inter-loge correlation terms $F(\Omega, \Omega')$ introduced by Bader²¹:

$$\begin{aligned} F(\Omega, \Omega') &= \int_{\Omega'} g_{\Omega}(r_1) dr_1 = N_{\Omega} \int_{\Omega'} \rho(r_1) dr_1 \\ &\quad - 2 \int_{\Omega'} dr_1 \int_{\Omega} \rho(r_1, r_2) dr_2 \end{aligned} \quad (10)$$

Having introduced the basic quantities, it is also now possible to specify briefly the methods of their analysis. Despite their being related to pair densities, the Fermi hole, whether from eq. (7) or eq. (5), is a one-electron quantity and as such can be analyzed by the same means and procedures as the ordinary electron density $\rho(r)$. One particularly useful method consists in the diagonalization of the matrix G_{Ω} , which represents the "charge-weighted" Fermi hole in eq. (7) in the AO basis. In our previous study,¹⁵ we have shown that, when the region Ω is identified with the region of a single isolated atom, the resulting Fermi hole [eq. (7)] can straightforwardly be interpreted in terms of valence state of the corresponding atom, and several examples of such an interpretation have been presented. These examples involved, however, only several trivial systems like CH_4 , NH_3 , H_2O , etc., in which the valence state of the central atom is well known. But, there are other more complex systems for which the exact picture of bonding is not very clear, such as hypervalent systems like SF_4 , SF_6 , PF_5 , BrF_5 , etc., which are of interest due to their lack of conformity to the Lewis octet rule. It was therefore of special interest for us to apply the aforementioned formalism to these hypervalent systems and to elucidate the bonding in them.

Computations

Although the noted methodology was formulated quite generally and can be applied at any level of theory, the practical applications discussed

in this study are based on some simplifying assumptions. The first of these concerns the pair density, which in our case was derived from semiempirical SCF wave functions generated by the AM1 method.²⁵ We are, of course, aware of the fact that, in view of the present standards, such an approach is rather crude, but we used it mainly because of the simplicity with which it can be implemented and subsequently tested at this particular level. Moreover, we believe, and the results indeed seem to warrant this belief, that even at this simple level the conclusions can be regarded as reliable enough and can certainly provide a good starting point prior to extensions to higher levels of theory. In addition to limiting ourselves to the semiempirical SCF level of theory there was yet another approximation used in practical testing. This approximation concerns the integration over Bader's atomic regions, which, because of the nonavailability of the programs for such an integration, was replaced by appropriately restricting the summations over the basis functions in the sense of Mulliken population analysis. Within this approach, which was also used in our previous studies,^{14,15} an electron is expected to be in the region of an atom A if it resides in a basis function centered on this atom. Thus, for example, the integrals over the atomic region of atom A of the type is approximated as:

$$2 \sum_i^{occ} \langle i|i \rangle_A = 2 \sum_i^{occ} \sum_{\mu}^A \sum_{\nu} c_{\mu i} c_{\nu i} S_{\mu\nu} \\ = \sum_{\mu}^A (PS)_{\mu\mu} = Q(A) \quad (11)$$

The above analysis was applied to wave functions describing the bonding in several hypervalent systems like SF₄, PF₅, SF₆, and BrF₅. The calculations were performed by the semiempirical AM1 method incorporated into the SPARTAN PC + ; program. Based on these primary data, the pair densities and corresponding Fermi holes were generated using our own FORTRAN program, which is available upon request. The molecules were in completely optimized molecular geometries. Experimental and calculated geometrical parameters are summarized in Table I. The agreement between experimental and theoretical parameters was not excellent in all cases (especially bond lengths), but for the qualitative demonstration of the applicability of the approach, the reproduction of basic structural parameters (including the bond angles) can be regarded as satisfactory.

Results and Discussion

Before examining the calculated Fermi holes, it is useful to summarize the state of knowledge of bonding in hypervalent molecules. Perhaps the best and the most competent discussion of this problem can be found in a relatively recent review by Gillespie and Robinson,²⁶ who critically reviewed all existing contradictory opinions and proposals. Thus, according to Musher,²⁷ the concept of hypervalence applies to nonmetals of the groups V, VI, VII, and VIII of the Periodic Table in any of their valence states other than their lowest stable valences 3, 2, 1, and 0, respectively. According to this definition, the species SF₄, PF₅, SF₆, BrF₅,

TABLE I.
Comparison of Experimental and AM1-Calculated Geometrical Parameters for a Series of Representative Hypervalent Molecules.

Molecule	Geometrical parameter	Experimental values (distance or angle)	Calculated values (distance or angle)
SF ₄	S—F _{ax}	1.646 Å	1.573 Å
	S—F _{eq}	1.545 Å	1.545 Å
	∠F _{eq} SF _{eq}	101.5°	103.8°
	∠F _{ax} SF _{ax}	173.1°	170.4°
SF ₆	S—F	1.564 Å	1.540 Å
PF ₅	P—F _{ax}	1.58 Å	1.549 Å
	P—F _{eq}	1.53 Å	1.535 Å
BrF ₅	Br—F _{eq}	1.774 Å	1.799 Å
	Br—F _{ax}	1.689 Å	1.823 Å
	∠F _{ax} BrF _{eq}	84.5°	85.2°

ClF_3 , etc., in which there are more than four electron pairs around the central atom in the classical structural formula, ought to be considered hypervalent. In addition to this phenomenological scheme, Musher proposed to introduce an additional classification to distinguish between two types of hypervalent molecules. The hypervalent molecules of the first kind (HV_I), have been characterized as being formed from existing molecules by the addition of two collinear monovalent (or single divalent) ligands in a manner that preserves the structure of the original molecule. This class of molecules includes SF_4 , ClF_3 , XeF_2 , BrF_5 , etc. Hypervalent molecules of the second type (HV_II) have been characterized as being formed from existing molecules by the addition of two monovalent (or single divalent) ligands accompanied by deep reorganization of the electron and geometrical structure with the resulting equilibrium geometry primarily governed by steric factors. Molecules like PF_5 , SF_6 , IF_7 , or XeO_4 belong to class HV_II , and they usually display the highest possible symmetry (octahedron in SF_6 , trigonal bipyramid in PF_5 , pentagonal bipyramid in IF_7 , etc.).

To explain the violation of the Lewis octet rule in hypervalent systems, the concept of d-orbital participation in hybridization was invoked initially,²⁸ but this explanation is now considered to be incorrect. The rejection of the idea of d-orbital participation comes mainly from the results of modern *ab initio* calculations in which it was shown that d-orbitals play the role of polarization functions without a major contribution to bonding. Another general observation from these calculations is that of the considerable ionic character of bonding in these systems. Based on this ionicity, a reinterpretation of the original Lewis octet rule was proposed^{29,30} in which only electrons in the valence shell of the central atoms are to be taken into account instead of including unspecified electron pairs that may be fully or partially shared or unshared in the original model. The ionic nature and polarization of some bonds lowers considerably the number of electrons in the valence shell of the central atom, and the octet rule is no longer violated, and these systems are to be regarded as "normal." However, this picture of bonding is also not completely satisfactory. For example, the existence of six bond paths in Bader's analysis in SF_6 and related systems³¹ clearly suggests that there are six bonds around the central atom in these molecules. Consistent with this picture are the results of recent sophisticated post-HF calculations³²⁻³⁵ in which the so-called "democracy prin-

ciple" was formulated. According to this principle, (almost) all electrons of central atoms can engage in bonding if provided with a sufficient energetic incentive. The electrons of the central atom originally residing in formally doubly occupied free electron pairs decouple and each of the resulting singly occupied orbitals takes part in bonding with a singly occupied orbital of the ligand. Electron correlation is responsible for this phenomenon. This means that such decoupling can be specifically detected in calculations in which electron correlation is properly taken into account. This was demonstrated in spin-coupled calculations,³²⁻³⁴ and in application of the GVB method, in which Messmer examined the importance of radial and angular correlation of lone pairs on bonding.³⁵ In this connection it is of interest to note that the same idea of decoupling free electron pairs was already considered by Musher,²⁷ but the demonstration of decoupling was impossible at the level of the qualitative MO model with which he worked. The phenomenon thus found its manifestation in the form of three-center four-electron bonds and it is just this three-center bonding that is characteristic of all *ab initio* calculations restricted to the SCF level of theory.²⁹

In view of what has been noted, this means that the model of three-center four-electron bonding consistent with the existing *ab initio* calculations should thus be regarded only as a projection of the bonding situation biased by the neglect of the electron correlation in SCF methods. On the other hand, when electron correlation is taken into account, the problem of hypervalent bonding seems instead to be consistent with the picture of an expanded octet (duodecet) rule.

Having outlined the present state of the theory of hypervalence, we now present the conclusions of our analysis. It is necessary to note that the Fermi holes generated in this report came from HF pair densities; therefore, a systematic bias from the HF approximation is likely to be reflected in our conclusions. The model is, however, simple enough to estimate the possible effects of including the electron correlation.

As already stated, the approach is based on the analysis of "charge-weighted" Fermi holes associated with the central atom of the hypervalent system. The Fermi holes satisfy:

$$\int g_\Omega(r_1) dr_1 = N_\Omega \quad (12)$$

which ensures the natural normalization of the hole to the total number of electrons in Ω . In the case in which the region Ω is associated with a single atom, the normalization factor is simply equal to the electron density on the atom in the molecule. This characterization is, however, rather crude and says nothing about any internal distribution of electrons on the atom. In a previous study¹⁴ we demonstrated that useful additional information can be extracted from the analysis of eigenvalues and eigenvectors of the matrix G_Ω representing the Fermi hole [eq. (7)] in the AO basis. For example, the diagonalization of the Fermi hole associated with the carbon atom in CH_4 yields only four nonzero eigenvalues. The degeneracy of these eigenvalues ($\eta_1 = \eta_2 = \eta_3 = 0.903$, $\eta_4 = 1.222$) suggests that the corresponding eigenvectors transform according to T_2 - and A_1 -irreducible representations of the T_d group. This, however, is inconsistent with the classical picture of four equivalent tetrahedrally oriented free valences. The equivalence can be obtained if the primary eigenvectors resulting from the diagonalization are subjected to the isopycnic transformation assessed by Cioslowski.³⁶ The result of this transformation, which leaves the Fermi hole invariant, is the final picture of the valence state, which indeed shows four equivalent tetrahedrally oriented sp^x -hybridized orbitals corresponding to free valences of broken CH bonds, with the occupation numbers $\eta_1 = \eta_2 = \eta_3 = \eta_4 = 0.982$ (Fig. 1). The occupation numbers of these free valences are close to 1 because the polarity of CH bond is low. This can be

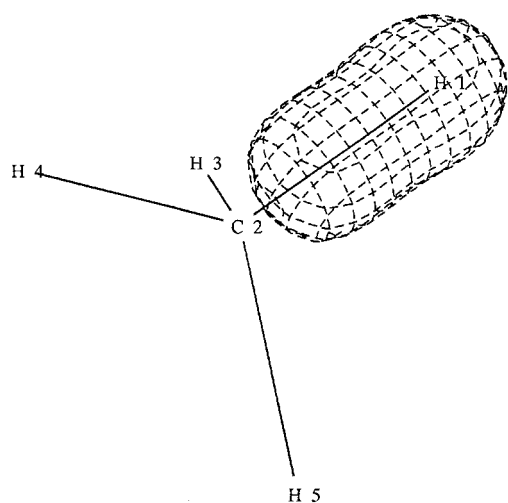


FIGURE 1. Eigenvector of the Fermi hole associated with the C atom in CH_4 . Eigenvector with the eigenvalue 0.982 corresponds to the nonpolar, broken C—H bond.

easily demonstrated by diagonalizing the Fermi hole associated with one of the hydrogens. This diagonalization yields one nonzero eigenvalue equal to 1.018, which exactly complements the population of free valence of broken CH bond to yield a nearly nonpolar two-center two-electron CH bond. In a similar way, the analysis of the Fermi hole of the N atom in NH_3 also yields four nonzero eigenvalues. One of them is equal to 2.000 and the remaining three are 1.076. Inspection of the form of associated eigenvectors shows that they correspond to a free electron pair on N and three tetrahedrally oriented free valences of broken NH bonds, respectively. Diagonalizing the Fermi hole associated with one of the hydrogens confirms the identification of the NH bonds as two-center two-electron bonds. The diagonalization yields one nonzero eigenvalue equal to 0.924, complementing the population of broken free valence to complete the nearly evenly shared one-bonding electron pair.

The simple cases in the previous paragraph strictly follow the Lewis octet rule. The remainder of this study presents the application of the same approach to more complex hypervalent systems. The resulting picture of the valence state of the central atom is compared with existing theories of hypervalence.

SF₄

SF_4 , whose structure is shown in Figure 2, belongs to the hypervalent system of type HV_1 which, according to Musher,²⁷ exhibits two types of bonds. One of them corresponds to two equatorial SF bonds and resembles normal covalent bonds. On the other hand, the axial SF bonds are quite different, and are classified as real hypervalent bonds. Let us compare this expectation with the actually computed results. In this analysis, the main focus will be on the nature of the valence state of the central hypervalent S atom. The diagonalization of the Fermi hole associated with this atom yields four nonzero eigenvalues. One of these eigenvalues is equal to 2.00 and inspection of the corresponding eigenvector shows that it corresponds to free electron pair on S (Fig. 3). There is a degenerate pair of eigenvalues equal to 0.694 and one eigenvalue equal to 0.677. Detailed inspection of the associated eigenvectors assigns the degenerate pair to two broken valences of equatorial SF bonds (Fig. 4), and the remaining eigenvector is very much a pure p orbital on S (Fig. 5). The deviation of the eigenvalues from unity can be interpreted as

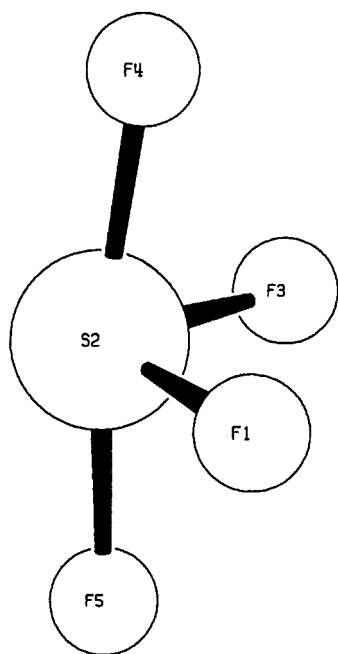


FIGURE 2. Schematic structure of the SF_4 molecule.

indicating highly polar SF bonds. This interpretation is again supported by the analysis of the Fermi holes associated with equatorial fluorine atoms. There are eight nonzero eigenvalues (2×4) of which six (corresponding to free electron pairs on fluorines) are equal or very close to 2 and the

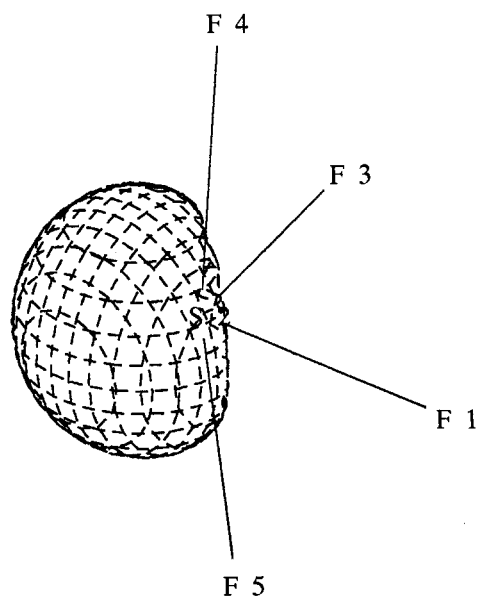


FIGURE 3. Eigenvector of the Fermi hole associated with the S atom in SF_4 . Eigenvector with the eigenvalue 2.000 corresponds to free electron pair on sulfur.

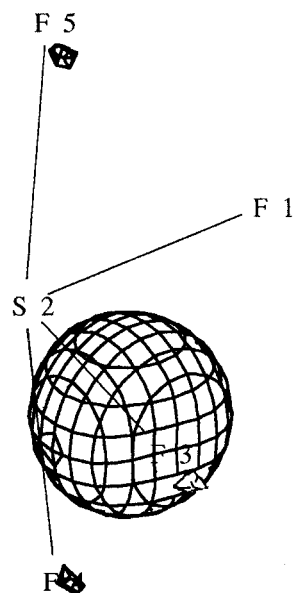


FIGURE 4. Another eigenvector of the Fermi hole associated with the S atom in SF_4 . Eigenvector with the eigenvalue 0.694 corresponds to one of the broken polar equatorial SF bonds.

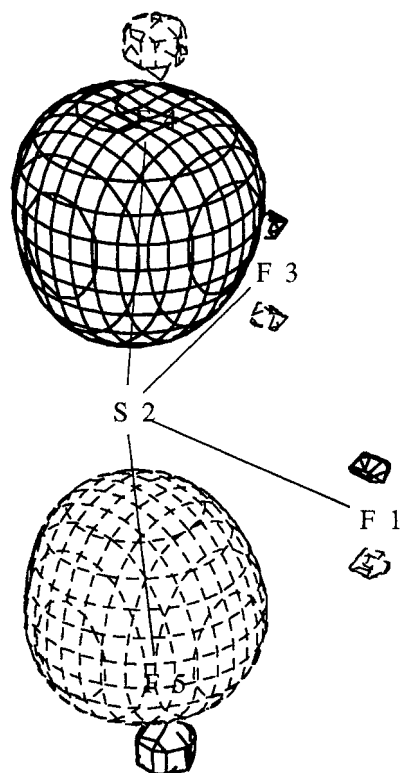


FIGURE 5. Another eigenvector of the Fermi hole associated with the S atom in SF_4 . Eigenvector with the eigenvalue 0.677 corresponds to the nearly pure p orbital on S, which participates in two polar axial SF bonds.

remaining two (corresponding to free valences of broken equatorial SF bonds) are equal to 1.512 each. The electron pairs in equatorial SF bonds are shared much less symmetrically than in the case of CH or NH bonds, consistent with the picture of highly polar bonds with considerable reduction of the charge on S. Except for this higher polarity, these SF bonds are quite normal σ bonds, which may be expected on the basis of Musher's analysis.²⁷

Having analyzed the equatorial SF bonds, let us turn our attention to the axial SF bonds. The eigenvalue equal to 0.677 is associated with an eigenvector that looks like a pure p orbital on S. This result is noteworthy because there are *two* axial SF bonds. This implies that the partially populated *single* p orbital on S has to be engaged in *two* axial SF bonds. This result is very important for at least two reasons. First, there is a close correspondence with the classical model by Hasch and Rundle³⁶ and Pimentel,³⁸ implying the existence of three-center four-electron bonding. The presence of three-center four-electron bonds predominantly localized in axial SF bonds is also confirmed by the values of three-center bond indices^{11,39} (Table II). The second reason is that the axial SF bonds are even more polar than the equatorial ones. To demonstrate this, we compare the eigenvalue of 0.677 corresponding to the partially populated p orbital on S with the eigenvalues resulting from diagonalization of the Fermi hole associated with two axial fluorines. This diagonalization yields eight nonzero eigenvalues of which six are close to 2.00 (free electron pairs on fluorines), and the remaining two are equal to 1.658 each. Taking into

account that the partially populated p orbital on S in fact participates in two bonds, the effective population per one such bond should be $0.677/2 \approx 0.338$. This again nearly perfectly complements the population on individual fluorines to give the picture of two unevenly shared electron pairs in two axial SF bonds. By artificially halving the population of the p orbital on S, one can model qualitatively the effect of decoupling anticipated by Musher²⁷ and reflected in the form of angular correlation³⁵ in a more sophisticated post-HF calculation. Despite being based on the HF level of theory, the picture of bonding in this type of hypervalent molecule can thus support surprisingly well conclusions from modern post-HF calculations that incorporate the expansion of the valence shell over the classical Lewis octet.

BrF₅

Another example of the HV_I-type of hypervalent molecule is bromine pentafluoride, BrF₅. The structure of this molecule is a slightly distorted square pyramid (Fig. 6), and the calculated equilibrium geometry corresponds to this type of structure. The main focus in discussing the bonding of BrF₅ will be on the analysis of the valence state of the central Br atom in terms of its associated Fermi hole. The diagonalization of this hole again yields four nonzero eigenvalues. One of them is equal to 2.00 and, in addition to another one equal to 1.111, there is a degenerated pair of eigenvalues equal to 0.986. Inspection of the corresponding eigenvectors shows that eigenvalue 2.00 is associated with a σ -free electron pair on Br opposite to the axial BrF

TABLE II.
Calculated Values of Three-Center Bond Indices in Several Hypervalent Molecules.

Molecule	Three-center bond	Number of symmetry equivalent indices	Multicenter bond index ^a
SF ₄	F _{ax} SF _{ax}	1	−0.082
	F _{eq} SF _{eq}	1	−0.054
	F _{ax} SF _{eq}	4	0.000
BrF ₅	F ₃ BrF ₄	2	−0.141
	F ₁ BrF ₃	4	−0.052
	F _{eq} PF _{ax}	6	−0.034
PF ₅	F _{eq} PF _{eq}	3	−0.015
	F _{ax} PF _{ax}	1	−0.010
	F ₁ SF ₄	12	−0.039
SF ₆	F ₁ SF ₃	3	−0.024

^aNegative values of three-center bond index indicate three-center four-electron bonding limiting value for ideal three-center four-electron bond is −0.187.¹¹

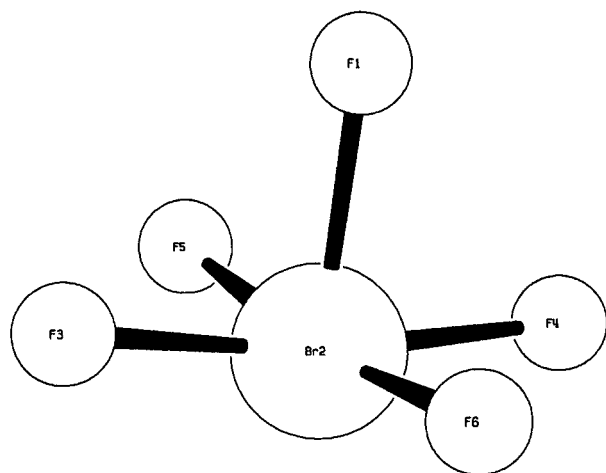


FIGURE 6. Schematic structure of the BrF_5 molecule.

bond. Eigenvalue 1.111 corresponds to an eigenvector representing the free valence of the broken axial BrF bond. This bond is similar in many respects to equatorial SF bonds in SF_4 with the exception of lower polarity. Analysis of the Fermi hole associated with the axial fluorine confirms this finding. Diagonalization again yields four nonzero eigenvalues of which three are close or equal to 2, corresponding to free electron pairs on F, whereas the remaining value is equal to 1.223, representing the orbital of broken axial BrF bond.

The degenerate pair of eigenvalues corresponds to eigenvectors representing nearly pure p_x and p_y orbitals on bromine. The situation in which two partially populated p orbitals have to participate in four BrF bonds is analogous to the case of axial bonds in SF_4 . This situation implies the existence of three-center four-electron bonds, and these bonds (localized predominantly in the F_3BrF_4 and F_5BrF_6 bonds) can indeed be detected using three-center bond indices (Table II). Another noteworthy aspect of equatorial BrF bonds is their relatively higher polarity compared with the axial BrF bond. This polarity may seem surprising, because the eigenvalues corresponding to p_x and p_y orbitals participating in these bonds are equal to 0.986; however, as in the case of axial SF bonds in SF_4 , one should recall the fact that each of the p orbitals participates in two bonds. The effective population per one formal bond should thus be close to $0.986/2 \approx 0.493$. This picture is also consistent with the analysis of the Fermi holes associated with equatorial fluorines. The analysis yields 16 (4×4) nonzero eigenvalues, of which 12 (3×4), corresponding to free pairs on fluorines, are close to

2.00. The remaining four, corresponding to free valences of broken BrF bonds, are equal to 1.510. The populations in free valences on Br and F of broken equatorial BrF bonds complement each other quite closely, to give the final picture of four polar two-center two-electron bonds.

PF_5

An example of a hypervalent system of type HV_{II} is PF_5 . Following Musher's²⁷ reasoning, we expect that formation molecules of this type require deep electron and geometrical reorganization yielding the highest possible symmetry as the most stable structure. This is the case with PF_5 which is a trigonal bipyramid with axial bonds slightly longer than the equatorial ones. This difference has been qualitatively well reproduced by the calculations (Table I). In analyzing the bonding in this molecule, the main focus will be on the analysis of the valence state of the central phosphorus atom. The diagonalization of the Fermi hole associated with this atom again yields four nonzero eigenvalues, of which three are equal to 0.551 and the remaining one equal to 0.481. Detailed inspection of the form of individual eigenvectors shows that triply degenerate eigenvectors correspond to free valences of three equatorial PF bonds (Fig. 7), and the remaining resembles a pure p orbital oriented

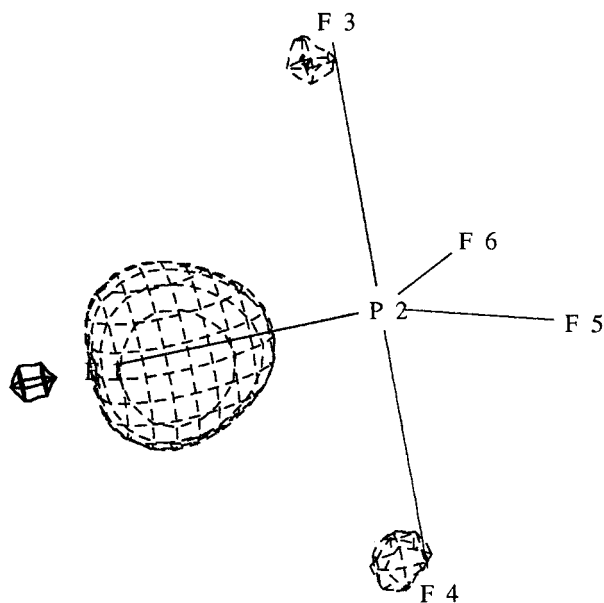


FIGURE 7. Eigenvector of the Fermi hole associated with the P atom in PF_5 . Eigenvector with the eigenvalue 0.551 corresponds to one of the broken polar equatorial PF bonds.

along axial PF bonds (Fig. 8). The situation is similar to that of SF_4 in which a single partially populated p orbital was also shown to participate in two axial bonds. Despite this parallel, there is an important difference. In HV_{II} -type molecules, the central atom uses all its valence electrons in bonding so that it attains its maximal possible valence. This, of course, also presumes decoupling of all available free electron pairs, but because these molecules display the highest possible symmetry, the decoupling is accompanied by deep electron reorganization on the central atom. As a result of this reorganization, the coexistence of pseudocovalent equatorial and three-center four-electron axial bonds characteristic of HV_{I} molecules is no longer tenable, and all PF bonds become more or less equivalent. This conclusion is supported by the values of three-center bond indices (Table II), which suggest that the three-center bonding present here is much weaker than for genuine three-center four-electron bonds. The molecule ought to be regarded as composed of five more or less equivalent polar PF bonds. However, one should note that the expansion of the octet is indicated only indirectly by the absence of

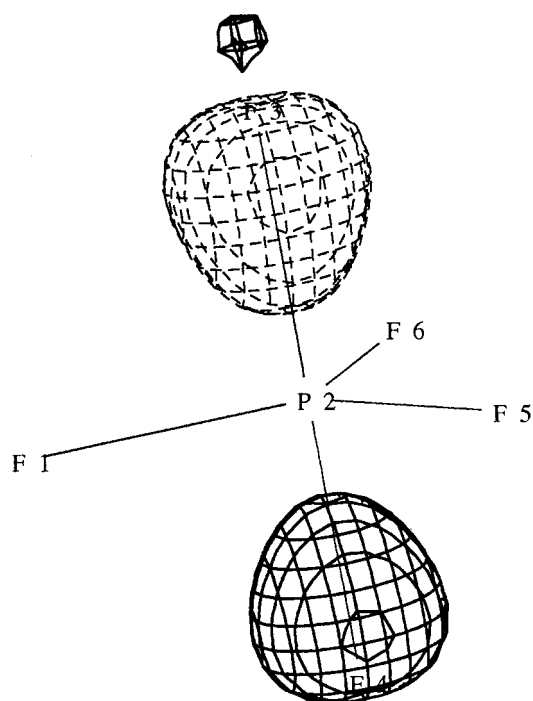


FIGURE 8. Another eigenvector of the Fermi hole associated with the P atom of PF_5 . Eigenvector with the eigenvalue 0.481 corresponds to nearly pure p orbitals of phosphorus, the decoupling of which is required for the formation of two polar axial PF bonds.

localized three-center four-electron bonding and by the near equivalency of all five PF bonds. The expansion of the octet can, in real molecules, again be attributed to decoupling of the electron pair in a partially populated p orbital. Because electron correlation, which is responsible for this decoupling in real molecules, is not taken into account in HF pair densities, the explicit demonstration of this expansion lies outside the scope of the present approach. We believe, however, that when electron correlation is properly taken into account, the formalism just examined would be able to detect the octet expansion directly.

SF_6

Another example of the HV_{II} hypervalent molecule is sulfur hexafluoride, SF_6 . As is typical for this class of systems, all valence electrons participate in bonding, implying deep electron and geometrical reorganization to attain the highest possible symmetry. Consistent with this expectation, the molecule exists in the form of a regular octahedron with all SF bonds equal in length. The analysis begins again with diagonalization of the Fermi hole associated with the S atom. Four nonzero eigenvalues are found in two degenerate pairs equal to 0.773 and 0.677, respectively. The eigenvectors associated with the first pair of eigenvalues correspond to sp^x hybrids of axially oriented free valences of two broken SF bonds. One of these eigenvectors is visualized in Figure 9. The

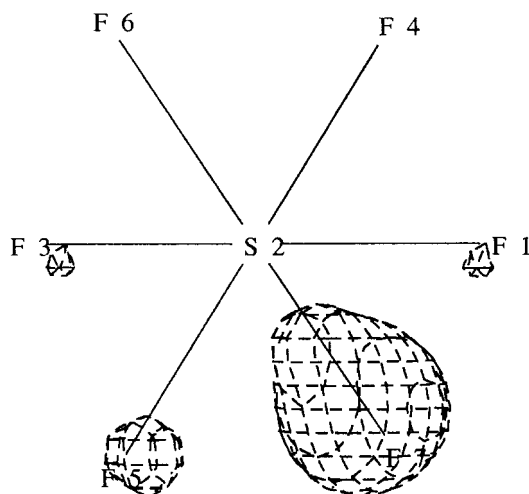


FIGURE 9. Eigenvector of the Fermi hole associated with the central S atom in SF_6 . Eigenvector with the eigenvalue 0.773 corresponds to one of two broken polar SF bonds.

remaining two eigenvectors resemble equatorially oriented pure p orbitals that are engaged in four remaining SF bonds, and one of the symmetry equivalent pairs of these eigenvectors is shown in Figure 10. Such a picture of bonding is reminiscent of what we have met previously with the PF_5 molecule. Comparable to what is characteristic of HV_{II} -type systems, the decoupling of each of the individual p orbitals required for the expansion of the valence shell is accompanied by deep electron reorganization, allowing the molecule to adopt the high observed symmetry. As a consequence of this electron reorganization, there is thus no difference between individual SF bonds, and all these bonds are strictly equivalent and display a quite small three-center character. We can thus again see the difference between HV_{I} - and HV_{II} -type hypervalent systems. Whereas, in HV_{I} molecules, the decoupling of more or less pure p orbitals in two bonds is projected at the HF level in the presence of three-center four-electron bonding, the situation in HV_{II} systems is different, and in keeping with the presence of deep electron reorganization the final picture of bonding is consistent with the observed high symmetry, with all bonds completely or nearly equivalent. This can be demonstrated easily by inspecting Table II, in which the values of multicenter bond indices are not only consistent with the observed high symmetry, but

also are considerably smaller than for genuine three-center four-electron bonds.

The picture of bonding presented here explains and rationalizes the results of even much more sophisticated calculations surprisingly well. One question that arises is whether the fact that four, and only four, nonzero eigenvalues are always found in the diagonalization of the Fermi hole associated with the heavy atom, is related to the low flexibility of the AM1 basis set which involves only one s and three p orbitals. The answer to this question is "no," because essentially the same results are obtained if analogous calculations are repeated using the semiempirical SINDO method⁴⁰ in which d orbitals are involved on the atoms of the second row. As Table III shows, the only result of including d orbitals in the basis is the appearance of additional nonzero eigenvalues (two in PF_5 and five in SF_6 , which are, however, much smaller than the four original eigenvalues. This is consistent with the generally accepted conclusion that d orbitals play only a negligible role in hypervalent bonding.

Acknowledgment

The authors also thank one of the referees for helpful suggestions.

TABLE III.
Comparison of Eigenvalues of Fermi Holes
Generated by AM1 and SINDO Methods to
Demonstrate the Minor Role of d-Orbitals
in Basis Set.

Molecule	AM1	SINDO
SF_6	0.773	1.160
	0.773	0.837
	0.659	0.721
	0.659	0.715
		0.295
PF_5		0.289
	0.551	0.678
	0.551	0.626
	0.551	0.630
	0.481	0.610
		0.193
		0.109
		0.109
		0.073
		0.073

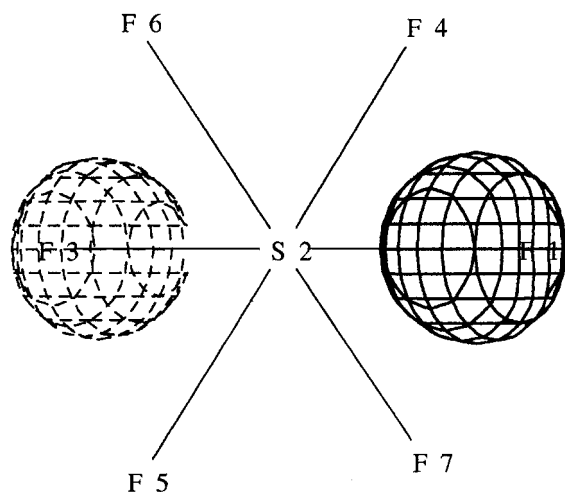


FIGURE 10. Another eigenvector of the Fermi hole associated with the S atom in SF_6 . Eigenvector with the eigenvalue 0.667 corresponds to one of the two nearly pure orbitals on S, the decoupling of which is required to form two other SF bonds. The remaining two such bonds result from the decoupling of the second symmetry-equivalent p orbital on S.

References

1. Coulson, C. A. *Proc R Soc* 1939, A169, 413.
2. Wiberg, K. B. *Tetrahedron* 1968, 24, 1083.
3. Mayer, I. *Int J Quantum Chem* 1984, 26, 151.
4. Jug, K. *J Am Chem Soc* 1977, 99, 7800.
5. Cioslowski, J.; Mixon, S. T. *J Am Chem Soc* 1991, 113, 4142.
6. Gopinathan, M. S.; Jug, K. *Theor Chim Acta* 1983, 63, 497, 511.
7. Jug, K. *J Comput Chem* 1984, 5, 555.
8. Ponec, R.; Strnad, M. *Int J Quantum Chem* 1994, 50, 43.
9. Ponec, R.; Bochicchio, R. *Int J Quantum Chem* 1995, 54, 99.
10. Ponec, R.; Uhlik, F. *J Mol Struct (Theochem)* 1997, 391, 159.
11. Ponec, R.; Mayer, I. *J Phys Chem* 1997, 101, 1738.
12. Ponec, R.; Jug, K. *Int J Quantum Chem* 1996, 60, 75.
13. Bochicchio, R.; Ponec, R.; Uhlik, F. *Inorg Chem* 1997, 36, 5363.
14. Ponec, R. *J Math Chem* 1997, 21, 323.
15. Ponec, R. *J Math Chem* 1998, 23, 85.
16. Wigner, E.; Seitz, F. *Phys Rev* 1933, 43, 804.
17. Boyd, R. J.; Coulson, C. A. *J Phys B* 1974, 7, 1805.
18. Luken, W. L.; Beratan, D. N. *Theor Chim Acta* 1982, 61, 265.
19. Luken, W. L. *Croat Chem Acta* 1984, 57, 1283.
20. Cooper, I. L.; Pounder, C. N. M. *Theor Chim Acta* 1973, 47, 51.
21. Bader, R. F. W.; Stephens, M. E. *J Am Chem Soc* 1975, 97, 7391.
22. Doggett, G. *Mol Phys* 1977, 34, 1739.
23. Bader, R. F. W. *Atoms in Molecules, a Quantum Theory*; Clarendon Press: Oxford, UK, 1994.
24. Ruedenberg, K. *Rev Modern Phys* 1962, 14, 326.
25. Dewar, M. J. S.; Zoebish, E. G.; Hailey, E. F.; Stewart, J. J. P. *J Am Chem Soc* 1985, 107, 3902.
26. Gillespie, R. J.; Robinson, E. A. *Inorg Chem* 1995, 34, 978.
27. Musher, J. J. *Angew Chem Int Ed* 1969, 8, 54.
28. Kwart, H.; King, K. G. *d-Orbitals in Chemistry of Silicon, Phosphorus and Sulphur: Reactivity and Structure*, Vol 3; Springer: Berlin, 1977.
29. Reed, E. A.; Schleyer, P. v. R. *J Am Chem Soc* 1990, 112, 1434.
30. Cioslowski, J.; Mixon, S. T. *Inorg Chem* 1993, 32, 3204.
31. Robinson, E. A. *J Mol Struct (Theochem)* 1989, 9, 186.
32. Cunningham, T. P.; Cooper, D. L.; Gerratt, J.; Karadakov, P.; Raimondi, M. *Int J Quantum Chem* 1996, 60, 393.
33. Cooper, D. L.; Cunningham, T. P.; Gerratt, J.; Karadakov, P.; Raimondi, M. *J Am Chem Soc* 1994, 116, 4414.
34. Cooper, D. L.; Gerratt, J.; Raimondi, M. *J Chem Soc Perkin Trans* 1989, 2, 1187.
35. Patterson, C. H.; Messmer, R. P. *J Am Chem Soc* 1990, 112, 4138.
36. Cioslowski, J. *Int J Quantum Chem* 1990, S24, 1833.
37. Pimentel, G. C. *Physics* 1951, 19, 446.
38. Hach, R. J.; Rundle, R. E. *J Am Chem Soc* 1951, 73, 4321.
39. Ponec, R.; Uhlik, F. *Croat Chem Acta* 1996, 69, 941.
40. Nanda, D. N.; Jug, K. *Theor Chim Acta* 1980, 57, 95.